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PYRENE-DERIVED GRIGNARD REAGENT(S): PREPARATION AND USE IN KEY CARBONYLATION/CARBOXYLATION REACTIONS

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Abstract. Among traditional pyrene-containing derivatives, carbonyl/carboxyl compounds are important organic dyes/components, and their photophysical properties have been well studied[1]. Due to the high photoluminescence quantum yield[2] and the ability to form stable donor-acceptor complexes with electron deficient compounds, including nitroaromatic ones[3], pyrene derivatives are used as monomolecular chemosensors for the detection of nitro-explosives in solutions[4]. For the producing advanced materials, for instance based on graphene/graphene oxide, pyrenecarboxylic acid is widely used to develop new methods for the surface functionalization[5].

We have developed the atom-economical synthesis of pyrene-1-carbaldehyde **3**, pyrene-1-carboxylic acid **4** through 1-pyrenmagnesium bromide (Grignard reagent) derived from 1-bromopyrene[6] with moderate to high yields under mild conditions, as important synthons in order to obtain pyrenecontaining compounds with desired properties(Fig.1).

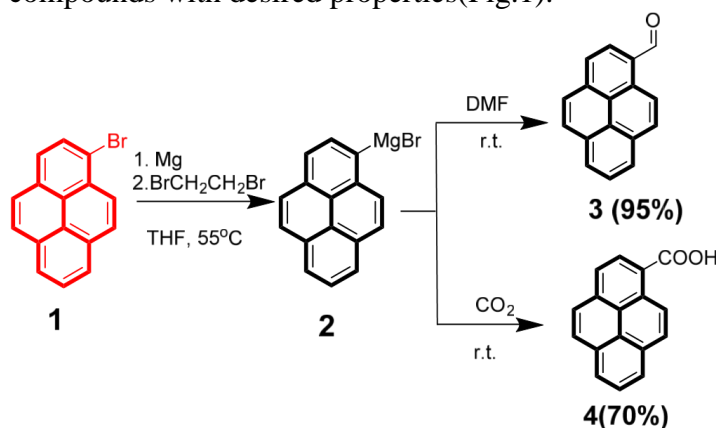


Figure 1. Scheme of synthesis of pyrene-1-carbaldehyde **3** and pyrene-1-carboxylic acid **4**

The chemical structures of compounds **3-4** are confirmed by ¹H and ¹³C NMR spectroscopy, mass spectrometric data and elemental analysis.

References

1. Niko Y. et al. Fundamental photoluminescence properties of pyrene carbonyl compounds through absolute fluorescence quantum yield measurement and density functional theory // Tetrahedron. Elsevier Ltd, 2012. Vol. 68, № 31. P. 6177–6185.
2. Berlman I.B. Handbook of fluorescence spectra of aromatic molecules. Academic Press, 1971. 473 p.
3. Barnes J.C. et al. Complexes of pyrene with 2,4,6-trinitroanisole. Studies of association in solution and the crystal structure of the 1:1 complex // Tetrahedron. 1984. Vol. 40, № 9. P. 1595–1601.
4. Kovalev I.S. et al. Fluorescent Detection of 2,4-DNT and 2,4,6-TNT in Aqueous Media by Using Simple Water-Soluble Pyrene Derivatives // Chem. - An Asian J. John Wiley & Sons, Ltd, 2016. Vol. 11, № 5. P. 775–781.
5. Prasad C., et al. An overview of graphene oxide supported semiconductors based photocatalysts: Properties, synthesis and photocatalytic applications // J. Mol. Liq. Elsevier, 2019. P. 111826.
6. Mitchell R.H., Lai Y.-H., Williams R. V. N-Bromosuccinimide-dimethylformamide: a mild, selective nuclear monobromination reagent for reactive aromatic compounds // J. Org. Chem. 1979. Vol. 44, № 25. P. 4733–4735.